J. Am. Chem. Soc. **1989**, *111*, 2875-2882

Catalytic Dimerization of Ethylene and Propylene by (η^6-Arene)NiR$_2$ and in Combination with Alkylaluminum Halides. Production of Highly Active Homogeneous Catalysts

Seok-Burm Choe, Hiroyoshi Kanai, and Kenneth J. Klabunde*

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. *Received August 29, 1988*

Abstract: A series of (η^6-arene)NiR$_2$ and (η^6-arene)CoR$_2$ (R = SiF$_3$, SiCl$_3$, C$_6$F$_5$; arene = benzene, toluene, mesitylene) complexes were examined for activity as homogeneous catalysts for ethylene and propylene dimerization. Very high activities were encountered especially for M = Ni and R = SiCl$_3$. Kinetic analyses were carried out showing approximately first-order dependence on ethylene and Ni catalyst. Reaction rate changes with variation showed the following: in arene, benzene > toluene > mesitylene; with change in R, SiCl$_3$ $\gg$ SiF$_3$ > C$_6$F$_5$; with change in M, Ni $\gg$ Co. A mechanism and catalytic cycle are proposed, suggesting a Ni–H species as a key catalytic intermediate and the rate-determining step as production of the Ni–H species by Ni–Si bond breaking and elimination of RCH=CH$_2$. Addition of a Lewis acid cocatalyst EtAlCl$_2$ had a dramatic effect, causing even higher dimerization rates and longer catalyst lifetimes. Extensive multinuclear NMR studies suggested the formation of a (η^6-arene)Ni(SiCl$_3$)$_2$·4EtAlCl$_2$ adduct where Si–Cl bonds were converted to Si–Et species. With the cocatalyst system propylene could also be dimerized rapidly but with more rapid catalyst degradation. Mechanistic proposals for the effect of EtAlCl$_2$ are given.

Ziegler reported in 1954 the so-called "nickel effect" whereby a small amount of nickel could mediate C$_2$H$_4$ insertion into the Al–C bond of Et$_3$Al so that the product was 1-butene, rather than polyethylene.[1] Since this report, other workers have reported on a variety of transition-metal systems in combination with alkylaluminums and alkylaluminum halides as catalysts for C$_2$H$_4$ dimerization. Among the early transition metals, titanium and zirconium alkoxides[2–4] and halides[5,6] showed the highest activity for dimerization, oligomerization, and polymerization reactions. Among the later transition metals, most of the published work deals with Ni complexes. Ligands such as acetylacetonato,[7] olefins, dienes,[8] η^3-allyl groups,[9] and others have been employed. High activities for dimerization or oligomerization have been realized but usually in combination with Lewis acids such as alkylaluminum halides.[9,10] Activity in the absence of Lewis acid is rare, although there are some systems that have been investigated.[11,12]

Mechanistic investigations have also been reported,[9,10,13–15] but the complexity of these cocatalyst systems has made it difficult to gain the clear understanding desired.

Table I. Dimerization of Ethylene with (η^6-Arene)NiR$_2$[a]

			product ratio,[c] %		
catalysts	max rate[b]	N_t, s^{-1}	1-Bu	*cis*-2-Bu	*trans*-2-Bu
(η^6-benzene)Ni(SiCl$_3$)$_2$	1.5	0.025	32.6	41.6	25.8
(η^6-toluene)Ni(SiCl$_3$)$_2$	1.4	0.023	38.1	39.3	22.6
(η^6-mesitylene)Ni(SiCl$_3$)$_2$	0.8	0.013	42.8	37.2	20.6
(η^6-toluene)Ni(SiF$_3$)$_2$	0.14	0.0023	78.7	11.8	9.5
(η^6-toluene)Ni(C$_6$F$_5$)$_2$	0.09	0.0015			

[a] The reaction was carried out in bromobenzene solvent at 0 °C, 200 Torr ethylene constant pressure, and 5 × 10^{-3} M initial nickel concentrations. See Experimental Section for details. [b] Units: mol of ethylene consumed/mol of catalyst·min. [c] 1-Bu = 1-butene. *cis*-2-Bu = *cis*-2-butene. *trans*-2-Bu = *trans*-2-butene.

During our investigations of a new class of Ni complexes, i.e. (η^6-arene)NiR$_2$ (R = SiF$_3$, SiCl$_3$, C$_6$F$_5$),[16–18] we have discovered that these materials possess extremely high activities for 1-butene isomerization[19] as well as ethylene and propylene dimerization in the absence of a cocatalyst. And, addition of a cocatalyst increases their activities and lifetimes. Herein, we report our investigations of the dimerization process, *both with and without cocatalyst*. We have investigated both homogeneous systems as well as a heterogenized (polystyrene)NiR$_2$ system. Throughout this work we hoped to gain evidence of catalytically active intermediates and evidence regarding the role of the cocatalyst.

Results

I. **(η^6-Arene)NiR$_2$ Monocatalyst System (No Cocatalyst).** Our first series of experiments were designed to lend understanding of the effect of structural modification to **1**

$$CH_2{=}CH_2 \xrightarrow[0\ ^\circ C,\ \text{solvent}]{(\eta^6\text{-arene})NiR_2\ \text{catalyst}} CH_2{=}CHCH_2CH_3 + cis/trans\text{-}CH_3CH{=}CHCH_3$$

on the rate of ethylene dimerization. Kinetic analyses were carried

---

(1) (a) Ziegler, K. *Brennst.-Chem.* **1954**, *35*, 321. (b) Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 943.

(2) Martin, H. *Angew. Chem.* **1956**, *68*, 306.

(3) Cesca, S.; Marconi, W.; Santostasi, M. L. *J. Polym. Sci., Part B* **1969**, *7*, 547.

(4) Naatta, G. *J. Polym. Sci.* **1959**, *34*, 151.

(5) Langer, A. W. *J. Macromol. Sci., Chem.* **1970**, *4*, 775.

(6) Attrige, C. J.; Jackson, R.; Maddock, S. J.; Thompson, D. P. *J. Chem. Soc., Chem. Commun.* **1973**, 132.

(7) Jones, J. R.; Symes, T. J. *J. Chem. Soc. C* **1971**, 1124.

(8) Onsager, O. T.; Wang, H.; Blindheim, U. *Helv. Chim. Acta* **1969**, *52*, 187.

(9) Bogdanovic, B.; Henc, B.; Karmann, H. G.; Nussell, H. G.; Walter, D.; Wilke, G. *Ind. Eng. Chem.* **1970**, *62*, 34.

(10) (a) Maruya, K.-i.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2255. (b) Ishimaru, Y.; Maruya, K.-i.; Nakamura, Y.; Mizoroki, T.; Ozaki, A. *Chem. Lett.* **1981**, 657. (c) Su, C. L.; Collette, J. W. *J. Organomet. Chem.* **1972**, *36*, 177. (d) Olive, O. H.; Olive, S.; Schmidt, E. *J. Organomet. Chem.* **1972**, *39*, 202. (e) Bogdanović, B.; Spliethoff, B.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 622. (f) Onsager, O. T.; Wang, H.; Blindheim, U. *Helv. Chim. Acta* **1969**, *52*, 187.

(11) A series of catalysts prepared by SHOP (Shell High Olefin Process) showed high activity without aluminum cocatalysts.

(12) (a) McClure, J. P.; Barnett, K. W. *J. Organomet. Chem.* **1974**, *80*, 385. (b) Keim, W.; Hoffmann, B.; Lodewick, R.; Peuchert, M.; Schmitt, G.; Fleischhaver, J.; Meier, U. *J. Mol. Catal.* **1979**, *6*, 79. (c) Keim, W.; Kowaldt, F. H.; Goddard, R.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466.

(13) Onsager, O. T.; Wang, H.; Blindheim, U. *Helv. Chim. Acta* **1969**, *52*, 230.

(14) Jones, J. R. *J. Chem. Soc. c* **1971**, 1117.

(15) Sen, A.; Lai, T. W. *Organometallics* **1983**, *2*, 1059.

(16) Lin, S. T.; Narske, R. N.; Klabunde, K. J. *Organometallics* **1985**, *4*, 571.

(17) Groshens, T. J.; Klabunde, K. J. *J. Organomet. Chem.* **1983**, *259*, 337.

(18) Janikowski, S. K.; Radonovich, L. J.; Groshens, T. J.; Klabunde, K. J. *Organometallics* **1985**, *4*, 396.

(19) Kanai, H.; Choe, S. B.; Klabunde, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 2019.

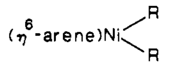
0002-7863/89/1511-2875$01.50/0

Table II. Solvent Effects on Ethylene Dimerization Reactions[a]

solvent	rate[b]	N_t, s^{-1}	product ratio,[c] % 1-Bu	 *trans*-2-Bu	 *cis*-2-Bu
iodobenzene	1.4	0.023	10.0	76.9	13.1
bromobenzene	1.4	0.023	31.6	42.9	25.5
chlorobenzene	0.14	0.0023	54.6	28.6	17.1
fluorobenzene	0.05	0.00083	68.4	21.1	10.5
toluene	0.001	0.000016	46.4	39.3	14.3
methylene chloride	<0.0001	0.0000016			

[a] See details in the Experimental Section: catalyst, (η^6-mesitylene)-Ni($SiCl_3$)$_2$; $P_{CH_2=CH_2}$, 200 Torr; T, 0 °C. [b] Units: mol of product/mol catalyst·min. [c] The products were analyzed after the end of the reactions.

out at constant ethylene pressure, concentration of **1**, solvent, and temperature. Only the structure of **1** was varied.



1. η^6-arene = benzene, toluene, mesitylene

A. Variation in η^6-Arene (π-Arene Effect) (R = $SiCl_3$). Reaction rates corresponding to different arene complexes are shown in Table I (R = $SiCl_3$). We can see that the general reaction patterns are similar for each arene, but the rate of the dimerization varies slightly in the order benzene > toluene > mesitylene. This finding is in accord with the lability of the η^6-arene determined in previous work from our laboratory.[20-22] That is, more electron-rich arenes bind to Ni more strongly and are less labile, and this leads to less active catalysts. This result is also in agreement with our earlier work on 1-butene isomerization.[19]

Product distributions derived from the benzene, toluene, and mesitylene complexes are also shown in Table I, varied only slightly, but the mesitylene system gave the best selectivity to 1-butene. More active catalysts generally gave poorer selectivity to 1-butene.

B. Variation in R (R = SiF_3, $SiCl_3$, C_6F_5). While η^6-arene was kept the same (toluene), the R groups were varied and kinetic analyses of the dimerization again carried out.[23] In these experiments we observed very large reaction rate differences (Table I). Obviously, the catalytic process is very sensitive to the nature of R. The activity order is R = $SiCl_3 \gg SiF_3 > C_6F_5$. Also, we noted that the induction period to reach maximum reaction rate was shorter for R = $SiCl_3$ (6 min for $SiCl_3$; 10 min for SiF_3 and C_6F_5).

C. Solvent Effect. Solvent effects in alkene dimerization reactions can be dramatic.[9,19,24-26] However, systematic studies have rarely been reported. Our earlier work showed that solvent does have an important role,[19] and this is especially true in ethylene dimerization.

Table III. Effect of [Ni] and $P_{CH_2=CH_2}$ on the Ethylene Dimerization Reaction

[Ni],[a] M	1.4×10^{-3}	2.8×10^{-3}	3.8×10^{-3}	5.2×10^{-3}
rate[b]	3.0×10^{-3}	5.0×10^{-3}	7.5×10^{-3}	9.8×10^{-3}
$P_{CH_2=CH_2}$,[c] Torr	100	200	300	400
rate[b]	3.0×10^{-3}	5.7×10^{-3}	8.0×10^{-3}	11.0×10^{-3}

[a] [Ni]: The concentration of (η^6-mesitylene)Ni($SiCl_3$)$_2$ with 200 Torr $CH_2{=}CH_2$ pressure, 0 °C, bromobenzene. $P_{CH_2=CH_2}$: The pressure of ethylene in a 5×10^{-3} M [Ni], 0 °C, bromobenzene solution. [b] Calculated for 1 L of solution at given concentration. Unit: mol of product/L of solution·min. [c] (η^6-mesitylene)Ni($SiCl_3$)$_2$ was held at 5×10^{-3} M, 0 °C, bromobenzene solution.

Table IV. Effect of [Ni] and $P_{CH_2=CH_2}$ on the Ethylene Dimerization Reaction by (η^6-Mesitylene)Ni($SiCl_3$)$_2$/$AlEtCl_2$ Cocatalyst

[Ni],[a] M	1×10^{-4}	2×10^{-4}	3×10^{-4}	4×10^{-4}
rate[b]	2.5×10^{-2}	4.9×10^{-2}	9.0×10^{-2}	13.0×10^{-2}
$P_{CH_2=CH_2}$,[c] Torr	100	200	300	400
rate	2.0×10^{-2}	3.5×10^{-2}	5.5×10^{-2}	8.0×10^{-2}

[a] The aluminum cocatalyst concentration was 1.8×10^{-2} M for these experiments. As [Ni] was varied $P_{CH_2=CH_2}$ was held at 100 Torr. [b] Unit = mol of product/L of catalyst solution·min. [c] As $P_{CH_2=CH_2}$ was varied, [Ni] was held at 1×10^{-4} M.

We were not able to use alkane solvents due to the relative insolubility of **1** in these. Also, **1** reacts by arene displacement in ethers, sulfides, and other Lewis base solvents. Thus, we were restricted to arene solvents. Even so, large effects were observed (Table II). High activities were observed in bromo- and iodobenzene but much lower in chloro- and fluorobenzene. Also, the induction period was shortest for iodobenzene, but activity fell off faster.

We looked for evidence of η^6-arene/solvent exchange using NMR (π-complexed arenes in **1** exhibit substantial upfield shifts). No evidence for η^6-haloarene complexes was found. These results do not preclude an equilibrium where very small amounts of η^6-haloarene complex may be present but confirm our earlier work showing that the –NiR$_2$ moiety is very sensitive to electron density in the arene and greatly prefers more electron-rich systems. (The high lability of all the (η^6-arene)NiR$_2$ systems has been demonstrated by earlier work.)[21,22,27]

D. Rate Equation and Activation Energies. To obtain the rate equation, we studied the effects of the concentration of nickel complex **1**, ethylene pressure, and temperature (Table III). The general rate equation can be expressed by (1) where *a* and *b* are determined by experiment. Our results show that the rates were

$$\frac{d[\text{butenes}]}{dt} = k[CH_2{=}CH_2]^a[\mathbf{1}]^b \tag{1}$$

linearly proportional to ethylene pressure and concentration of **1** (plotting *the maximum rates attained vs* concentration (or pressure)). Due to the relatively short lifetimes of these catalysts, conventional log plots were not useable (although Lewis acid promoted systems exhibited long lifetimes; see later discussion). This approximate treatment allowed us to determine that *a* and *b* are about equal to 1.

Using this empirical rate equation (eq 2), we determined an approximate E_a by examining reaction temperature variations.

$$\frac{d[\text{butenes}]}{dt} = k[CH_2{=}CH_2][\mathbf{1}] \tag{2}$$

The rate constant *k* in (2) may not be the absolute value but should be proportional to the real value; see later discussion. An Arrhenius plot yields a E_a of 13 ± 3 kcal/mol.

We noted, however, at higher [Ni] concentrations (>10^{-2} M) and/or high pressures of C_2H_4 (>500 Torr) deviations from linearity.

II. (η^6-Arene)NiR$_2$/$EtAlCl_2$ Cocatalyst Systems. Most homogeneous catalysis studies of ethylene dimerization have been carried out with cocatalyst systems. Alkylaluminum halides have

---

(20) (a) Groshens, T. J.; Klabunde, K. J. *Organometallics* **1982**, *1*, 564. (b) Lin, S. T.; Groshens, T. J.; Klabunde, K. J. *Inorg. Chem.* **1984**, *23*, 1.

(21) Brezinski, M.; Klabunde, K. J. *Organometallics* **1983**, *2*, 1116.

(22) Choe, S. B.; Klabunde, K. J. *J. Organomet. Chem.* **1989**, *359*, 409–418.

(23) Syntheses of these compounds have been reported in ref 16 and the following: (a) Brezinski, M.; Klabunde, K. J.; Anderson, B. B. *Organomet. Synth.* **1986**, *3*, 158. (b) Choe, S. B.; Klabunde, K. J. *Organomet. Synth.* **1986**, *3*, 153. (c) Choe, S. B.; Klabunde, K. J. *Organomet. Synth.* **1986**, *3*, 156. (d) Lin, S. T.; Klabunde, K. J. *Organomet. Synth.* **1986**, *3*, 147.

(24) Olive, O. H.; Olive, S.; Schmidt, E. *J. Organomet. Chem.* **1972**, *39*, 202. Kawakami, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 21.

(25) Onsager, O. T.; Wang, H.; Blindheim, U. *Helv. Chim. Acta* **1969**, *52*, 196.

(26) Akhmedov, V. M.; Khanmetov, A. A.; Mardanov, M. A.; Zakharkin, L. I. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 442.

(27) Gastinger, R. G.; Anderson, B. B.; Klabunde, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 4959.

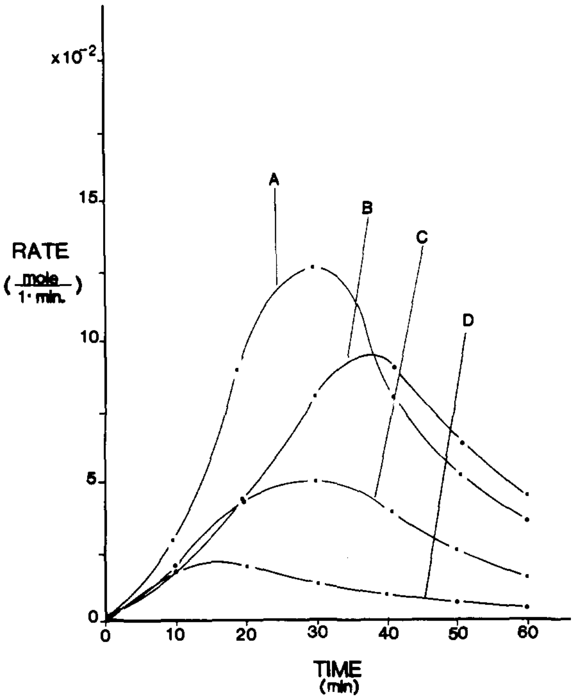


Figure 1. Time profiles/reaction rates for ethylene dimerization using **1** (arene = mesitylene) combined with $EtAlCl_2$ (concentration variations): (A) concentration of **1** = 1×10^{-4} M [Ni] and of [Al] = 1.8×10^{-2} M; (B) concentration of **1** = 2×10^{-4} M [Ni] and of [Al] = 1.8×10^{-2} M; (C) concentration of **1** = 3×10^{-4} M [Ni] and of [Al] = 1.8×10^{-2} M; (D) concentration of **1** = 4×10^{-4} M [Ni] and of [Al] = 1.8×10^{-2} M. Reactant = ethylene at 200 Torr pressure; solvent = bromobenzene; temperature = 0 °C.

Table V. Effect of [Al] on the Rate of the Ethylene Dimerization Reactions

[Al], M	[Ni], M	[Al]/[Ni]	max rate[a]	N_t, s^{-1}
7.2×10^{-2}	4×10^{-4}	180	5.8×10^{-2}	2.4
3.6×10^{-2}	4×10^{-4}	90	4.2×10^{-2}	1.8
1.8×10^{-2}	4×10^{-4}	45	4.1×10^{-2}	1.7
7.2×10^{-3}	8×10^{-4}	9	9.8×10^{-2}	2.0
3.6×10^{-3}	8×10^{-4}	4.5	10.2×10^{-2}[b]	2.1
1.8×10^{-3}	8×10^{-4}	2.2	2.0×10^{-2}[b]	0.42
0.9×10^{-3}	8×10^{-4}	1.1	1.2×10^{-2}[b]	0.25

[a] Unit = mol of product/L of catalyst solution·min. [b] These minimum rates were reached within 5 min and activities lost within 15 min.

frequently been used, but other Lewis acids such as BF_3–etherate, $AgClO_4$, and others have also.

We chose a typical cocatalyst for our studies, that of $EtAlCl_2$. We tested for catalytic activity of $EtAlCl_2$ under typical ethylene dimerization conditions and found no activity.[28] Then we used combination of $EtAlCl_2$ and **1** in a ratio of 5:1 [Al] to [Ni], where the concentration of **1** was the same as that used in the monocatalyst studies. We found that the reaction rate was too rapid to follow using our existing apparatus (see the Experimental Section). We were forced to use a much larger ethylene reservoir and to decrease the Ni complex concentration by 50-fold in order to obtain a reaction rate that could be monitored. Again, we investigated the effects of Ni complex concentration, ethylene pressure, and reaction temperature. We also investigated $EtAlCl_2$ concentration changes.

The effects of changing the concentration of Ni complex **1** ((mesitylene)$Ni(SiCl_3)_2$) are shown in Table IV and Figure 1. It can be seen that the rate maxima depended on concentration but also the induction period to reach these maxima changed. Compared with the monocatalyst system, rates increased greatly (up to 100-fold).

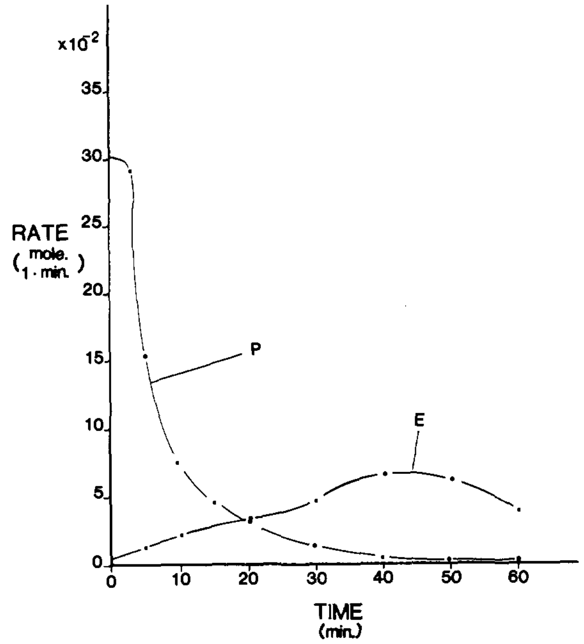


Figure 2. Time profiles/reaction rates for propylene and ethylene dimerization using **1** (arene = mesitylene) with $EtAlCl_2$: E = ethylene; P = propylene.

The $EtAlCl_2$ concentration effect is illustrated in Table V. At low [Al] to [Ni] ratios, the ethylene dimerization rate increased rapidly as this ratio changed from 1 to 4, but at high [Al]/[Ni] values (>10), the rate remained virtually the same.

Other reports of Lewis acid concentration effects reveal wide ranges of optimum Lewis acid/catalyst ratios from 1:1 to >100:1.[7,29] Also, in these reported systems, the dimerization rate decreased sharply once the optimum ratio was exceeded. However, in our system this was not found to be true; that is, not much change was observed at ratios >10:1. However, it is important to note that catalyst *lifetime* continued to increase as very high [Al] to [Ni] ratios were employed.

Studies of ethylene pressure changes showed that the dimerization rate changed linearly with pressure change (Table IV), and the time it took to reach the rate maxima was the same. These results are somewhat unusual since others have reported a second-order dependence on ethylene pressure (nonlinear).[30,31]

The relation between rate and ethylene pressure was quite reproducible and followed the first-order rate law. However, Ni concentration studies showed poor reproducibility, although averages of several experiments at each concentration did yield a reasonable first-order plot (first order in Ni complex and first order in ethylene).

III. Propylene Dimerization. Fewer nickel complexes are active for propylene dimerization, although several organonickel/aluminum halide combinations show activity.[8,9,10e,32-35] Of course we were interested in the behavior of **1** toward propylene and indeed found dimerization activity for the monocatalyst, although the rate was much lower than for ethylene dimerization. Interestingly, the induction period for reaching the maximum rate was much shorter for propylene (~2 min) than for ethylene (~20 min). Upon addition of the cocatalyst, reaction rates jumped to much higher values, exceeding even the ethylene dimerization rate

---

(28) Under our conditions $EtAlCl_2$ did not react with ethylene by Al–C insertion. At higher temperatures such reactions can occur.[15]

(29) Obeshchalova, N. V.; Feldblyum, V. S.; Pashchenko, N. M. *J. Org. Chem. USSR* (*Engl. Transl.*) **1968**, *4*, 982.

(30) Onsager, O. T.; Wang, H.; Blindheim, U. *Helv. Chim. Acta* **1969**, *52*, 224.

(31) Hojabri, F. *Erdoel Kohle* **1970**, *23*, 724.

(32) Baker, R.; Copeland, A. H. *J. Chem. Soc., Perkin Trans 1* **1977**, 2497.

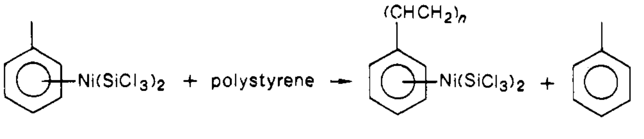
(33) Heimbach, P.; Kluth, K.; Schenkluhn, H.; Weimann, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 570.

(34) Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekern, F. J.; Mutterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 743.

(35) Pittman, C. U., Jr.; Smith, L. R. *J. Am. Chem. Soc.* **1975**, *97*, 1749.

for the cocatalyst system. This peculiarity regarding induction period remained the same, however. A rate/time profile is shown for the cocatalyst system (η^6-mesitylene)Ni($SiCl_3$)$_2$/$EtAlCl_2$ in Figure 2. Note that propylene dimerization proceeded very rapidly with essentially no induction period, but quickly dropped, while the ethylene dimerization rate continued to climb.

IV. Heterogenized Catalysts for Ethylene and Propylene Dimerization. When a toluene solution of **1** (arene = toluene; R = $SiCl_3$) is stirred with polystyrene, a polymer-attached catalyst was prepared.

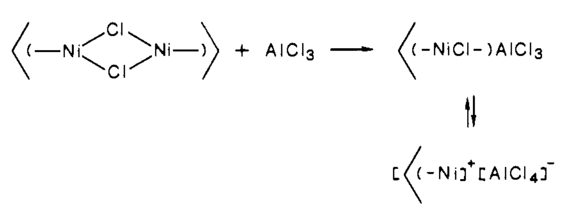


After toluene was removed, this catalyst was employed for dimerization reactions. High activities were encountered upon cocatalyst ($EtAlCl_2$) addition. Quantitative rate studies were not carried out. However, without $EtAlCl_2$ only about 2 mmol of ethylene was dimerized in 24 h, but with $EtAlCl_2$ more than 100 mmol was dimerized in 30 min. (See the Discussion for comparisons of turnover frequencies.)

As an aid in characterizing this heterogeneous catalyst, the relative amounts of Ni (by chelate/titration) and $SiCl_3$ groups (by acid/base titration methods) were determined. The ratio of $SiCl_3$/Ni was found to be 1.63, indicating that some $SiCl_3$ groups had been lost. Indeed, XPS studies of this catalyst (without cocatalyst) showed two peaks for Ni, one at 857.3 eV assigned to Ni(II) and another at 853.6 eV, which we believe could be due to Ni(I). The Si absorption at 103.0 eV was the same as the reference compound (we used (cyclophane)Ni($SiCl_3$)$_2$ as a reference).[22] The Cl absorption at 199.7 eV also was identical with the reference. It is interesting that the Ni to Si ratio was different from the reference, however, supporting our analytical results.

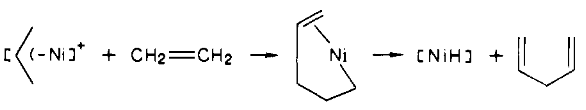
The (polystyrene)Ni($SiCl_3$)$_x$/$EtAlCl_2$ cocatalyst was active both in bromobenzene solvent (a slurry) or as a solid by itself without solvent.

V. Studies on the Cocatalyst Adduct. The spectacular response of Ni catalysts to organoaluminum compounds has drawn great interest from many laboratories; in particular, we note the work of Wilke,[9] Bogdanovic,[36] Heimbach,[33] and their co-workers. Onsager and co-workers[8,13,25,30] and Jones and Symes[7,15] should be mentioned. Investigations of the possible adduct structure for the η^6-allylnickel chloride/aluminum trichloride showed that the nickel dimer was broken up by $AlCl_3$ to form an equilibrium as shown below:

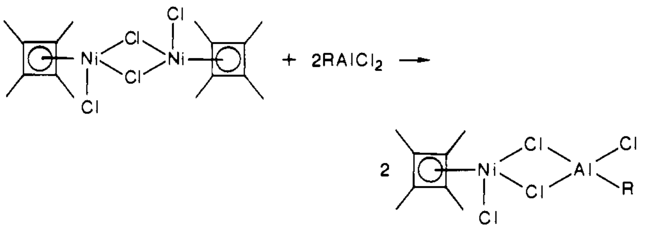


2

The structure of the adduct **2** was indirectly supported by the successful isolation of complexes such as η^6-$C_3H_5Ni(CO)AlX_4$, η^3-$C_3H_5(COD)AlX_4$, and others.[13,36] This adduct is believed to be the precursor to the actual catalyst, and the path to the actual catalyst was described as

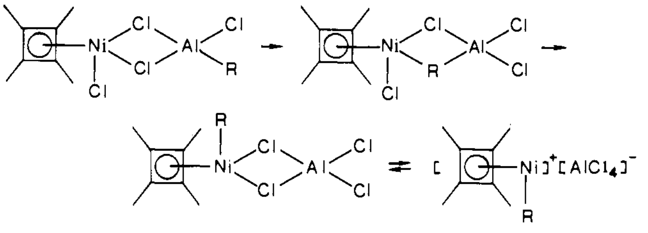


Onsager and co-workers[8,13,25,30] studied the tetramethylcyclobutadienenickel dichloride/$RAlCl_2$ system:



3

This adduct **3** did not behave as a catalyst precursor when $AlCl_3$ was the Lewis acid employed but did so when $EtAlCl_2$ was used. It was proposed that alkylation of nickel was necessary to generate the necessary precursor:

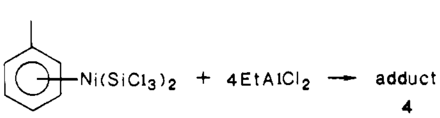


In these and other studies it was assumed that the transition-metal aluminum halide adduct was the catalyst precursor. The transition-metal complex was not active in its own right and did not serve as a precursor to the actual catalyst. Since they contained halide ligands through which the aluminum compound could interact, a useful precursor could be formed.

We now compare our (η^6-arene)NiR_2 systems. First, they are active in their own right for both ethylene and propylene dimerization. Second, they do not contain any nickel–halide bonds, yet when combined with $EtAlCl_2$, substantial catalytic activity increases are observed. Third, product distributions are quite different between the monocatalyst and cocatalyst systems. With monocatalyst, 60% 1-butene was formed, while with cocatalysts generally only about 2% 1-butene was formed.

With these considerations in mind, we began an investigation of the (η^6-arene)Ni($SiCl_3$)$_2$/$EtAlCl_2$ adduct from a structural point of view. Our most useful tool was multinuclear NMR.

The ^1H NMR spectra for the pure starting materials were compared with several [Al] to [Ni] adduct ratios. As the Al/Ni increased we saw new peaks appear in the arene region while the Et peaks no longer resembled those for $EtAlCl_2$. When the Al to Ni ratio was increased further, the relative intensities of these new peaks changed, and when the Al to Ni ratio exceeded four, peaks appeared that were at the same position at $EtAlCl_2$. Thus, we can conclude that the nickel complex reacted with $EtAlCl_2$, yielding a stable η^6-arene complex, which accommodated up to four molecules of $EtAlCl_2$.



4

The three new peaks in the arene region may correspond to three different η^6-arene complexes. We expect that two of them have a similar structure while one may be quite different, based on chemical shifts of 6.12, 6.05, and 5.80 ppm. Note, however, that as the Al to Ni ratio continued to increase, the arene peaks converged finally yielding one peak at 6.05 ppm.

We also used ^{13}C NMR and studied two samples, one with excess $EtAlCl_2$ and one without. Two peaks at the arene carbon region at 123.3 and 108.4 ppm correspond to π-bound mesitylene. When excess $EtAlCl_2$ was present, seven alkyl carbon peaks were observed, while only five were observed when the pure adduct **4** (no excess $EtAlCl_2$) was studied. Among these, the peaks at 8.3 and 3.9 ppm correspond to CH_2CH_3 in free $EtAlCl_2$, and the peak at 21.1 ppm corresponds to the methyl carbons bound to mesitylene. Four additional peaks at 23.4, 16.9, 8.1, and 6.9 ppm were

---

(36) Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 954.

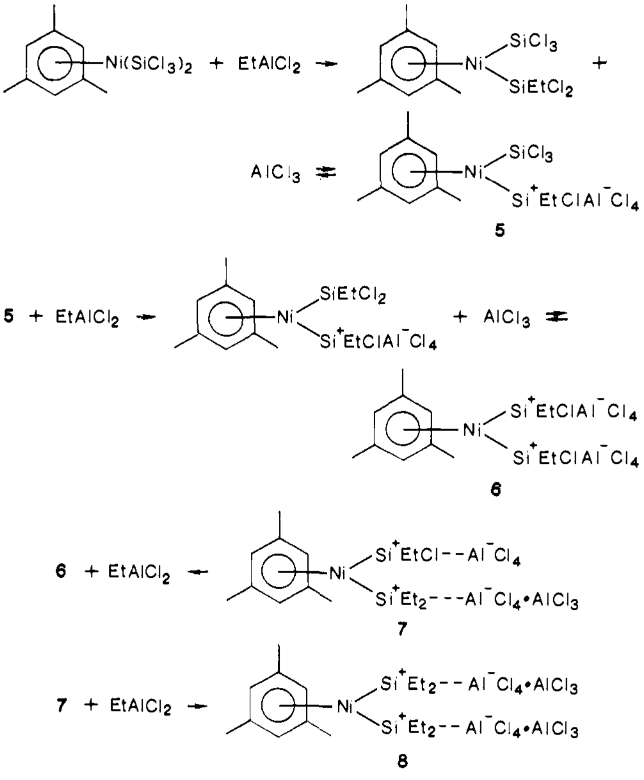
observed, and this indicates that two different kinds of Et groups exist in the adduct. These Et groups are not bound to Al since chemical shifts are different, and they are not broad as is observed in $EtAlCl_2$.

Another probe was ^{29}Si NMR.[37] The pure (η^6-mesitylene)$Ni(SiCl_3)_2$ has one ^{29}Si peak at 16.2 ppm relative to TMS. However, the adduct **4** has only one ^{29}Si peak at 111.0 ppm, which is 94.8 ppm downfield from that of the starting complex. It is clear that the environment for the Si atoms has changed a great deal.

Finally, ^{27}Al NMR[38] was employed and yielded very important information. The $EtAlCl_2$ was rather complex, suggesting that several species are in equilibrium, perhaps $Et_2AlCl/AlCl_3/EtAlCl_2$ as well as bridged species. Examination of adduct **4**, however, showed only two peaks, a very sharp one at 99 ppm (downfield from Al^{3+}/H_2O reference) and a broad one at 60 ppm. The sharp peak suggests a symmetrical structure, as the quadruple moment contribution causes ^{27}Al peaks to be broad unless in a symmetrical environment. The chemical shift and peak shape indicate that this 99 ppm peak is due to $AlCl_4^-$. The peak at 60 ppm could be due to $AlCl_3$ associated with solvent.[38,39] All these NMR data are collected in Table VI.

Adduct **4** heated in a high-resolution mass spectrometer probe yielded decomposition peaks as follows: 86.04 (40%), $SiEt_2^+$; 121.00 (89%), $SiEt_2Cl^+$. These data also show that alkylation of the $SiCl_3$ group took place, with SiEt groups as predominant species.

Using stoichiometry, NMR data, and MS data and needing to rationalize the effect of $EtAlCl_2$ on catalysis in our work, with the previous work of others in mind, we *propose* the following chemical reaction sequence:



Thus, adduct **4** may have a structure illustrated in **8**. When $EtAlCl_2$ is not in excess a mixture of **5–7** may be present, but these eventually convert to **8** upon further addition of $EtAlCl_2$. Note that **8** accommodates our need for four $EtAlCl_2$ molecules being used, the η^6-mesitylene remaining bound to Ni, and the NMR data for ^1H, ^{13}C, ^{29}Si, and ^{27}Al are all accommodated. Literature precedents are also available since it is known that alkylaluminum halides can alkylate halosilanes through an exchange process.[40] It is also known that halide can be abstracted from a silyl group bound to a transition metal.[41]

Table VI. NMR Data for the Complex Formed by the Reaction of (η^6-Mesitylene)$Ni(SiCl_3)_2$ and $AlEtCl_2$

	NMR values, ppm		
NMR	(η^6-mesitylene)-$Ni(SiCl_3)_2$	$AlEtCl_2$	adduct **4**
$^1H^a$	5.95 (s, 3 H)		6.00 (s, 3 H)
	2.04 (s, 9 H)		2.02 (s, 9 H)
		1.03 (t, 3 H)	1.40 (m, 5 H)
		0.40 (q, 2 H)	0.95 (m, 13 H)
$^{13}C^a$	124.9		123.3
	112.4		108.4
	20.7		21.15
		8.35	23.44
		3.95	16.90
			8.10
			6.98
$^{27}Al^b$		135	99.0
			60.0
$^{29}Si^b$	16.2		111.0

[a] In bromobenzene-d_5; reference was TMS. [b] In CD_2Cl_2; reference for Al was Al^{3+}; reference for Si was TMS.

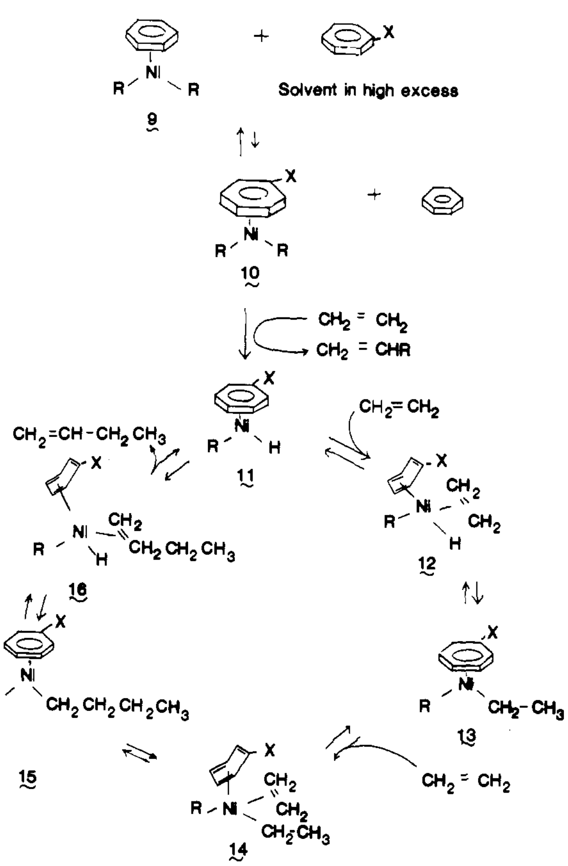


Figure 3. Proposed catalytic cycle for ethylene dimerization.

This adduct can be isolated as a yellow-orange liquid of limited thermal stability and high sensitivity to oxygen. So far we have not been successful in obtaining crystals for X-ray studies, which would be of considerable interest.

---

(37) Several good review papers on ^{29}Si NMR are available: (a) Williams, E. A. *Annual Reports on NMR Spectroscopy*; Academic Press: New York, 1983; Vol. 15, p 235. (b) Levy, G. C.; Cargioli, J. D. *Nuclear Magnetic Resonance Spectroscopy of Nuclei Other than Protons*; Academic Press: New York, 1976; p 251.

(38) Delpuech, J. J. *NMR of Newly Accessable Nuclei*; Academic Press: New York, 1983; Vol. 12, p 153.

(39) Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.

(40) Horder, J. R.; Lappert, M. F. *J. Chem. Soc. A* **1968**, 1167.

(41) Schmid, G.; Balk, H. J. *J. Organomet. Chem.* **1974**, *80*, 257.

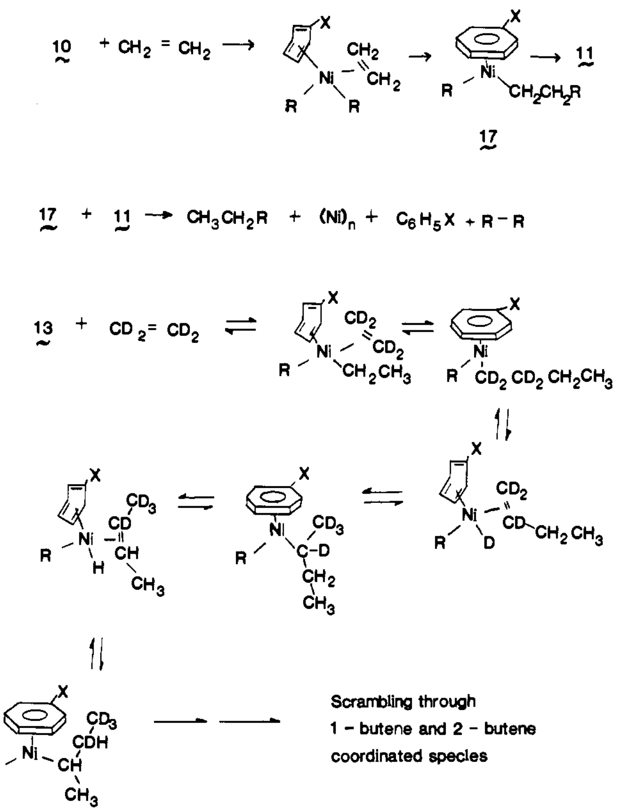


Figure 4. Proposed degradation steps and H/D exchange processes.

Discussion

I. **Monocatalyst System.** We propose the mechanism shown in Figure 3 with discussion of the steps involved to follow. Also, Figure 4 shows proposed catalyst degradation steps and H/D exchange processes.

First, the preequilibrium of **9** ⇄ **10** shown in Figure 3 will be considered. We know arenes in **9** that are most strongly bound give lowest catalystic rates, but the change from benzene to toluene to mesitylene is a noticeable but relatively small effect.[42] Now since all the arene–Ni bonds are very labile and since we observe a large solvent effect especially with bromobenzene (which is in very large excess), it seems reasonable that a prior equilibrium is operating. A small amount of the η^6-bromobenzene complex could be formed (although we cannot detect it by NMR) and should be an extremely active species and readily capable of shifting from $\eta^6 \rightarrow \eta^4$ with a low energy barrier. The extent of the formation of **10** should depend on the lability of the arene in **9**.

The conversion of **10** → **11** is obviously a critical step. Earlier we presented indirect evidence for the importance of **11** in 1-butene isomerization, based on H_2O and $CH_2{=}CH_2$ addition experiments and analysis of catalytic byproducts and degradation products, of which $CH_2{=}CHR$ is an important one.[19] We also have shown that $CD_2{=}CD_2/CH_2{=}CH_2$ mixtures yield H/D scrambled butenes, which would seem to necessitate Ni–H as an important species (see Figure 4). Since the **10** → **11** step required the breaking of the Ni–R bond, the strength of that bond should be a critical factor. Although we cannot quantify the argument, it is clear that the Ni–$SiCl_3$ bond would be weaker than the Ni–SiF_3 bond.[45] We have found that the difficulty in thermally decomposing these compounds is in the order of R = $SiF_3 \sim C_6F_5 > SiCl_3$. Thus, we believe that the Ni–C_6F_5 and Ni–SiF_3 bonds are considerably stronger than the Ni–$SiCl_3$ bond. Since the $NiSiCl_3$ system is a much more active catalyst than the other two, it is very likely that the **10** → **11** step *is rate determining*. This would also explain the kinetic results (first order in $CH_2{=}CH_2$ and **9**). We believe once **11** is formed ethylene dimerization takes place very rapidly through the equilibria shown in the cycle in Figure 3. However, there are significant degradation pathways for **11**, and examples are shown in Figure 4.

During the operation of the catalytic cycle, 1-butene is formed, but it may also be isomerized as demonstrated in the H/D exchange in Figure 4. However, 1-butene could be released and then reenter the reaction sphere to be isomerized, as an alternative. Since 1-butene isomerization has a very competitive rate vs ethylene dimerization, this latter idea certainly has merit.[19] We also recall that, in bromobenzene, 1-butene isomerization took place with no induction period, suggesting that the conversion of **10** to **11** (with 1-butene) was not the rate-determining step. Thus, for 1-butene isomerization the rate-limiting step lies within the catalytic cycle. It should be noted that **15** and **16** in Figure 3 are identical species that are involved in both 1-butene isomerization and ethylene dimerization. Table I shows the isomer distributions under various catalytic conditions. Note that the starting π-arene has a modest effect on the 1-butene fraction, the more catalytically active systems giving less 1-butene. Solvents have an even larger effect, the more reactive systems again giving less 1-butene. Finally, note that the effect of the R group (SiF_3 vs $SiCl_3$) is pronounced, the less active catalyst giving the largest 1-butene fraction. All these results suggest that 1-butene is the primary product, but its isomerization by **11** competes with ethylene dimerization. Thus, less active catalyst systems are more selective to 1-butene.

On first consideration, it may seem puzzling that a steric effect is not realized when 1-butene isomerization and ethylene dimerization are compared. Since it is not, this is further evidence that the rate-determining step is not within the catalytic cycle but instead is in the conversion of **10** → **11**. Also, it should be pointed out that steric congestion for 1-butene isomerization and ethylene dimerization would be about the same as when **14**–**16** are formed (**16** would be identical in both).

At this point propylene dimerization must be considered. We have not studied this system as extensively, but we do know that the dimerization rate is much lower. Steric effects must play a role in this case. Analogous structures for propylene as **14**–**16** would be considerably more sterically congested. It seems likely that the rate-determining step in the propylene case does involve one of these structures. Thus, the rate-determining step must change when ethylene is changed to propylene as feedstock, and it is possible when **13** → **14** (with propylene instead of ethylene) is that step.

One additional piece of evidence must be considered. Recall that the induction period for reaching maximum activity was shortened in the case of propylene compared with that of ethylene. This can be taken as a further suggestion that the rate step is not conversion of **10** → **11** (propylene) but may be conversion of **13** → **14** (propylene).

Our conclusions then are the following: (1) Formation of the Ni–H intermediate **11** (Figure 3) is rate limiting in ethylene dimerization in bromobenzene solvent. However, a prior equilibrium is operating such that a small amount of highly reactive (η^6-bromobenzene)Ni$(SiCl_3)_2$ complex is formed. (2) For propylene dimerization the rate-limiting step is formation of the

---

(42) This effect can be very large, however. Consider (η^6-toluene)Co$(C_6F_5)_2$ vs (η^6-toluene)Ni$(C_6F_5)_2$, which are isostructural.[43,44] The arene–Co bond is substantially shorter than the arene–Ni bond, and the arene in the latter shows some distortion due to an antibonding contribution from the extra electron on Ni (vs Co).[44] Thus, the arene–Ni bond is longer and weaker, and we believe this is a major factor in the Ni system being an active catalyst while the Co system is completely inactive under the same conditions.

(43) Ammeter, J. H.; Elschenbroich, C.; Groshens, T. J.; Klabunde, K. J.; Kuhne, R. O.; Mockel, R. *Inorg. Chem.* **1985**, *24*, 3307.

(44) Radonovich, L. J.; Koch, F. J.; Albright, T. A. *Inorg. Chem.* **1980**, *19*, 3373.

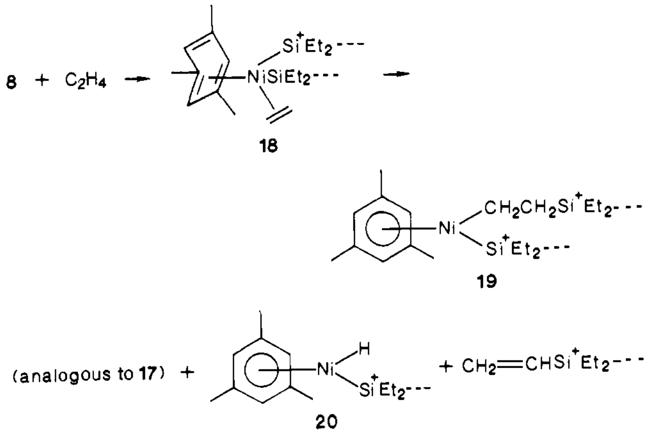
(45) No references were found for $NiSiF_3$, $NiSiCl_3$, and NiC_6F_5, but $HSiF_3$, $HSiCl_3$, and $HCoF_5$ were found: (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14(8)*, 246–62 (Cl_3SiH, 91.3 kcal/mol; F_3SiH, 100.1 kcal/mol). (b) Kreeh, M. J.; Price, S. W.; Yared, W. *Can. J. Chem.* **1974**, *52*, 2673–2678 (C_6F_5H, 152.1 kcal/mol).

(46) Keim, W.; Kowaldt, F. H. *Erdoel Kohle, Erdgas, Petrochem. Brennst.-Chem.* **1978**, *78–79*, 453.

sterically congested structures analogous to **14** and **15** (Figure 3, propylene). (3) The rate-limiting step in 1-butene isomerization in bromobenzene also lies within the catalytic cycle and is controlled somewhat by steric effects. We note that 1-butene isomerization is a faster process than ethylene dimerization, and therefore the most active catalysts yield the least selectivity for $2C_2H_4 \rightarrow$ 1-butene, since 1-butene can reenter the coordination sphere and be isomerized.

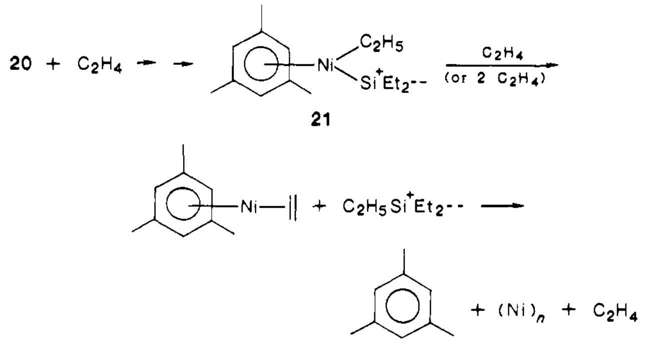
II. **Cocatalyst System.** Let us summarize the experimentally observed effects when $EtAlCl_2$ is added to the catalyst system: (1) Reaction rates are increased more than 100-fold for ethylene dimerization and 500-fold for propylene dimerization. (2) Catalyst lifetimes are greatly lengthened. (3) Induction periods were usually changed. (4) Large excesses of $EtAlCl_2$ further lengthen catalyst life.

Obviously the role of $EtAlCl_2$ is complex, and more than one chemical function is indicated. We assume that 4 mol of $EtAlCl_2$ form an adduct resembling **8**. Even lower rates of Al/Ni than 4 cause substantial rate increases. It would seem likely that, as $(\eta^6\text{-mesitylene})Ni(SiCl_3)_2$ is converted to **5** → **6** → **7** → **8**, any of these intermediate species is more capable of launching the catalytic cycle. Since **5–8** also possess a more electron deficient Ni center, ethylene may coordinate faster but, more importantly, be "silylated" faster:



If **19** is short-lived (shorter than **17**), conversion to **20** will be quicker, yielding the supposed catalyst intermediate faster. This might explain the increased rate. Furthermore, if the concentration of **19** is low at any moment (compared with **17** where no $EtAlCl_2$ is present), an important degradation pathway would be discouraged. This may explain the increased catalyst lifetimes.

A final question that we should deal with is why do *high excesses* of $EtAlCl_2$ further enhance catalyst lifetimes. We can only speculate concerning this. It may be that $EtAlCl_2$ weakly interacts with C_2H_4, cutting down on free C_2H_4 concentration. The $EtAlCl_2C_2H_4$ adduct could deliver C_2H_4 for the catalytic process, but a possible catalyst degradation pathway shown below might be minimized.



That is, free C_2H_4 may be more capable of driving the unwanted reductive elimination reaction. We recall that similar results were encountered with 1-butene isomerization; that is, high concentrations of 1-butene caused faster catalyst degradation.[19]

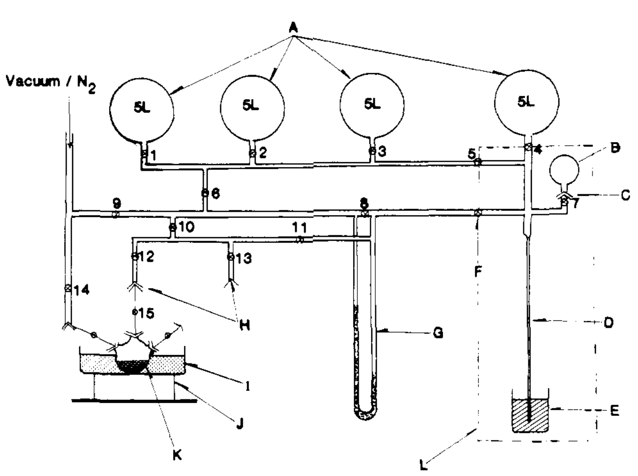


Figure 5. Ethylene/propylene dimerization apparatus. The lettered arrows refer to the following: (A) flasks for gas storage; (B) exchangeable flask (volume of the part L can be changed by this flask); (C) glass outlet (S/T 24/40 inner ground glass joint); (D) manometer (1-mm-i.d. capillary glass tube); (E) mercury pool; (F) needle valve; (G) manometer (6-nm-i.d. glass tube); (H) glass outlet (S/T 12/30 outer ground glass joint); (I) thermostat; (J) magnetic stirrer; (K) reaction vessel; (number) greaseless high-vacuum valves.

Similar arguments can be used to explain the results of propylene dimerization in the presence of $EtAlCl_2$. Recall that a very high rate of propylene dimerization was realized with almost no induction period. However, catalyst lifetime was very short. This could be explained by the fact that the solubility of propylene is much higher than ethylene in the solvent employed. Therefore, the concentration of propylene was very high, causing a rapid generation of catalytic species (NiH intermediate), but at the same time the high propylene concentration caused unwanted catalyst degradation pathways to be available. (We estimate the propylene concentration to be about 8×10^{-2} M while that of $EtAlCl_2$ was 2×10^{-2} M; even though this is a large amount of aluminum compound, still a great deal of free propylene would be available.)

Our conclusions then regarding rate steps when $EtAlCl_2$ is present are the following: (1) The formation of adduct **8** causes a quickening of the formation of the NiH active catalyst **11**, thereby shifting the rate-limiting step into the catalytic cycle. (2) Excess $EtAlCl_2$ seems to discourage catalyst degradation pathways, perhaps by mediating the delivery of ethylene to the catalytic center.

III. **Turnover Frequencies.** Of course, we do not know the number of molecules of true active catalyst present in the solutions at any chosen time. However, minimum turnover frequencies can be calculated by making the assumption that all the starting Ni complex is converted to active catalyst and by choosing the time (s^{-1}) when maximum reaction rate was observed. With these assumptions turnover frequencies (N, s^{-1}) were calculated and are collected in Tables I, II, and V.

The values shown are high for the cocatalyst systems. For comparison we can site the work of Keim and Kowaldt who report analogous values of about 0.1 s^{-1}.

For propylene dimerization over the cocatalyst, an N_t s^{-1} value of 1.0 is obtained at maximum rate. For $(polystyrene)Ni(SiCl_3)_2$ the N_t (s^{-1}) value for ethylene is 0.55 and propylene is 2.2, for comparison purposes.

Experimental Section

Materials. The toluene, benzene, mesitylene, methylene chloride, and halobenzenes were purchased from the Aldrich Chemical Co. or Fisher Scientific Co. and dried by refluxing overnight over P_2O_5 or CaH_2. The CD_2Cl_2, $CDCl_3$, and bromobenzene-d_5 were purchased from Aldrich Chemical Co. (purity 99.5% d) and were dried by refluxing overnight on P_2O_5 and stored under nitrogen after freeze/thaw degassing. The $(\eta^6\text{-arene})NiR_2$ (arene = mesitylene, toluene, benzene; R = $SiCl_3$, pentafluorophenyl) were prepared by following the procedures described elsewhere.[20,27] Ethylene and propylene were purchased from the Matheson Co. (purity 99.5%) and stored after freeze/thaw degassing and liquid nitrogen/dry ice fractional trap redistilling. Ethylaluminum dichloride was purchased from Aldrich Chemical Co. and used without further purification.

Apparatus. The reactions and measurements were carried out using apparatus shown in Figure 5. To obtain good kinetic data, it was important to control the pressure of gas and the temperature of the reaction mixture and to measure accurately the amount of gas used. These conditions could be met by making a slight modification of the usual vacuum line and thermostat and are described below. The apparatus consists of four 5-L flasks with condensing side fingers (A in Figure 5), one U-shaped manometer made from 6-mm-i.d. glass tube (G), one straight capillary manometer made with 1-mm-i.d. glass capillary tubing (D) with a Hg pool (E) at the bottom, one male outlet with S/T 22/40 ground glass joint (C), two female outlets with S/T 15/30 ground glass joint (H), one needle valve (F), and several greaseless high-vacuum valves (numbers in Figure 5). The four flasks were used to store gases. The gas pressure in the reactor could be monitored by reading the manometer G. The volume of section L, surrounded by a dotted line, was measured accurately and used as a constant volume gas reservoir. The pressure of this section L could be measured by reading the manometer D. As gas was consumed during the reaction, the pressure of the gas dropped and more gas was supplied to keep the pressure constant. To do this, it was necessary to keep the pressure of gas in reservoir L higher than that in the reactor. When the reactor gas pressure began to drop, the needle valve F was opened and thus supplied the proper amount of gas from the high-pressure reservoir L. The amount of gas supplied to the reactor during the reaction could be determined by measuring the change in the pressure of gas section L and multiplying it by the volume of this section. Since the amount of gas consumed during the reaction depended on the activity of the catalyst, the pressure change of the reservoir also depended on the activity of the catalyst. To reduce the reading error we used different reservoir volumes by connecting different size flasks B to outlet C. For monocatalyst systems we used a 100-mL flask, which made the total reservoir volume 176.0 ± 0.5 mL. For cocatalyst systems a 500-mL flask was used, which made the total reservoir volume equal to 595.5 mL. These values are the average of several measurements. With this device we could follow reactions as fast as 2.5×10^3 (mol of ethylene/mol of catalyst·min), and the measurement could be repeated within 3% relative error. Also the gas pressure of the reactor could be kept within ±1 mmHg variation. As a simple thermostat, we used a Dewar flask, which was an excellent insulator. During preliminary tests the Dewar kept the temperature of the reactor at 20 °C for more than 1 h. When we set the reactor at 10 °C, it changed 1° after 30 min. So, we could maintain the temperature setting throughout the reaction simply by adding small amounts of cold water or hot water to the Dewar flask and assumed that the temperature of the reactor was in equilibrium with the Dewar.

Reactions. 1. Ethylene Dimerization: Monocatalyst System. Using 0.05 mmol of (η^6-arene)Ni($SiCl_3$)$_2$ (arene = mesitylene, toluene, benzene), (η^6-toluene)Ni(SiF_3)$_2$, and (η^6-toluene)Ni(C_6F_5) as catalysts, ethylene dimerization reactions were carried out in 10 mL of desired solvent. We studied the effects of reaction parameters (arenes and ligands on nickel complex, solvents, nickel concentration, ethylene pressures, etc.) on the activity of the complexes. All manipulations were carried out under purified, dry nitrogen.

2. Ethylene Dimerization: Cocatalyst System. The arene nickel complexes showed catalytic activity, but their lifetimes were somewhat limited. To solve this problem, we tried the reaction using ethylaluminum dichloride as a cocatalyst. This cocatalyst system not only improved the lifetime but activity improved as well.

a. Reactions with Different Nickel Concentrations. Reactions were performed using cocatalyst with four different nickel concentrations: 1×10^{-4}, 2×10^{-4}, 3×10^{-4}, and 4×10^{-4} M. As catalysts, (η^6-mesitylene)Ni($SiCl_3$)$_2$ and ethylaluminum dichloride were used. For sample preparation and reaction conditions we followed the general procedure given above. All the reaction conditions were set the same as that of the ethylene reactions (T = 0 °C, P = 200 Torr, solvent = bromobenzene). The cocatalyst solution remained homogeneous throughout the reaction.

b. Reactions with Different Aluminum Concentrations. Seven samples were prepared for the reactions. Three samples had high [Al] to [Ni] ratios (180, 90, and 45), and four other samples had relatively low [Al] to [Ni] ratios (9, 4.5, 2.2, and 1.1). For samples where the [Al] to [Ni] ratios were low, a 4×10^{-4} M nickel concentration was used. For samples where [Al] to [Ni] ratios were high, a 2×10^{-4} M nickel concentration was used. Other reaction conditions were set the same as in a. When [Al] to [Ni] ratios were 1.1 and 2.2, the solution color changed from pale yellow to gray and showed low activity, whereas when the [Al] to [Ni] ratio reached 4.5, the color of the solution did not change and the activity increased substantially.

c. Reactions with Different Temperatures and Pressures. Reactions were performed under four different pressures (100, 200, 300, and 400 Torr). Other than pressure, we used the same reaction conditions as in a where the nickel concentrations were changed. In this case we used a 1×10^{-4} M nickel concentration. The behavior of the solution was similar in a and b. Another set of reactions were done with three different temperature (0, 10, and 20 °C). The reaction conditions were the same as before.

3. Propylene Dimerization. Three reactions were performed for propylene dimerization using (η^6-arene)Ni($SiCl_3$)$_2$ where the arenes were mesitylene, toluene, and polystyrene. The reaction conditions were the same as for the ethylene reactions (T = 0 °C, P = 200 Torr, propylene, solvent = bromobenzene, [Ni] = 1×10^{-4} M). The complex catalyzed the reaction, but the rate was not high enough for any meaningful kinetic measurements. Again we tried the cocatalyst for this reaction. The reaction conditions were the same as that in b. This cocatalyst system showed very high activity and reached a rate maximum within 2 min but lost activity faster than that in the ethylene system.

Preparation of (Polystyrene)Ni($SiCl_3$)$_x$. A 25-mL solution of (η^6-toluene)Ni($SiCl_3$)$_2$ (0.420 g, 1 mmol) in CH_2Cl_2 was treated with 10.4 g of polystyrene beads (macropare 20–50 mesh) and stirred for 24 h under N_2. During this period the original red-brown solution turned nearly colorless and the originally white polystyrene beads turned black. The polystyrene beads were filtered off and dried under vacuum. Analysis for Ni content was carried out by chelation by decomposing 1 g of complex in 5 mL of water. The black complex turned colorless, liberating HCl and nickel ion. The amount of HCl was determined by acid/base titration, and the amount of Ni ion was determined by chelate titration.

Catalysis with (Polystyrene)Ni($SiCl_3$)$_x$. Preparation of the hetergeneous catalyst was carried out by mixing 1.0 g of (polystyrene)Ni($SiCl_3$)$_2$ with 10 mL of 1 M $EtAlCl_2$ in hexane, followed by solvent and excess $EtAlCl_2$ evaporation under vacuum. The resultant black beads were used as is or with bromobenzene solvent in catalysis reactions.

Reaction between (η^6-Mesitylene)Ni($SiCl_3$)$_2$ and $AlEtCl_2$. A total of 0.448 g of (η^6-mesitylene)Ni($SiCl_3$)$_2$ was dissolved in 30 mL of mesitylene, and to the resulting red-brown solution was added 10 mL of 1 M solution of $AlEtCl_2$ in hexane. The resulting solution was freeze–thaw degassed and then allowed to reach room temperature. During warming the solution was stirred. Within 10 min, some oily droplets began to form and settle down at the bottom of the Schlenk tube. When the reaction time was completed, two liquid layers were formed in the Schlenk tube. The upper layer was solvent containing the unreacted $AlEtCl_2$, and the bottom layer was the product. The upper layer was syringed out, and the bottom layer was washed twice with 30 mL of pentane; the resulting pale orange oily product was dried under vacuum. It was soluble in CH_2Cl_2 and bromobenzene but insoluble in pentane. It was also soluble in $CHCl_3$, but the color of the solution turned purple. The $CHCl_3$ solution of the product showed more than 1000 times larger electrical conductivity than that of the starting materials. IR (neat, cm^{-1}): 400 (s), 450 (s), 490 (s), 550 (br s), 620 (s), 660 (s), 720 (vs), 815 (s), 965 (m), 985 (w), 1010 (s), 1030 (s), 1085 (w), 1160 (w), 1170 (w), 1210 (w), 1230 (m), 1405 (m), 1500 (m), 1550 (m), 3100 (m). NMR: see Table VI. MS: decomposition peaks are recorded in the text.

Acknowledgment. The support of the National Science Foundation is acknowledged with gratitude.

Registry No. 8, 119337-12-1; $AlEtCl_2$, 563-43-9; (η^6-benzene)Ni($SiCl_3$)$_2$, 89389-59-3; (η^6-toluene)Ni($SiCl_3$)$_2$, 80410-01-1; (η^6-mesitylene)Ni($SiCl_3$)$_2$, 100909-73-7; (η^6-toluene)Ni(SiF_3)$_2$, 88083-21-0; (η^6-toluene)Ni(C_6F_5)$_2$, 66197-14-6; ethylene, 74-85-1; propylene, 115-07-1; polystyrene, 9003-53-6.